

~~BEST AVAILABLE COPY~~

PCT

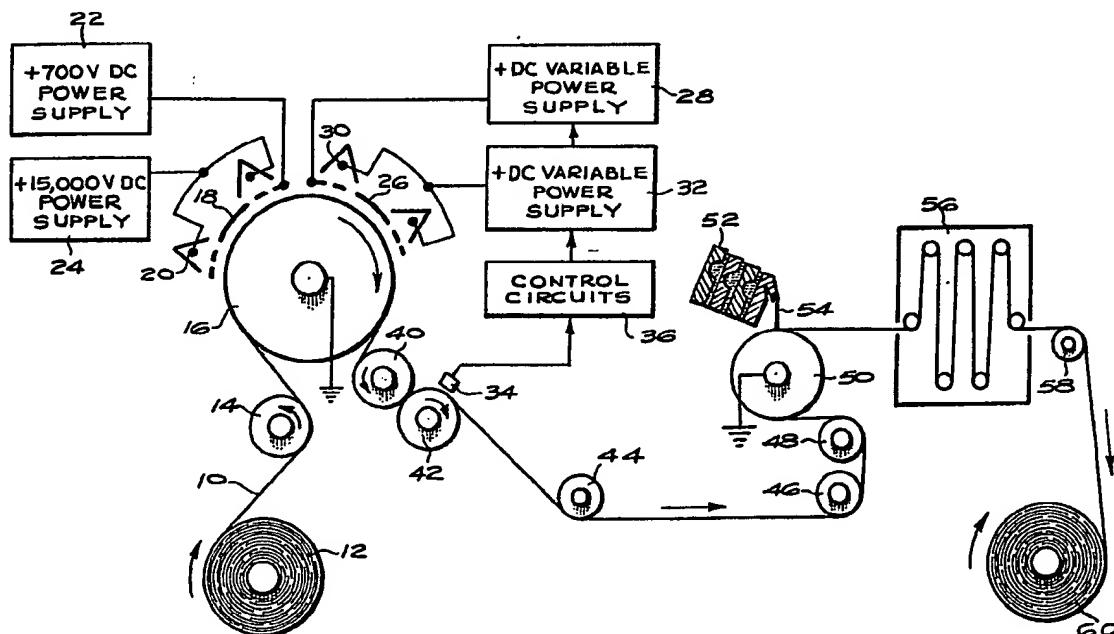
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : G03C 1/74, B05D 3/14 H05F 3/04	A1	(11) International Publication Number: WO 89/ 05477 (43) International Publication Date: 15 June 1989 (15.06.89)
(21) International Application Number: PCT/US87/03190 (22) International Filing Date: 3 December 1987 (03.12.87) (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventor: HARTMAN, Ronald, L. ; 133 Alcott Road, Rochester, NY 14626 (US). (74) Agent: TURNER, John, B.; 343 State Street, Rochester, NY 14650 (US). (81) Designated States: BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent).		Published <i>With international search report.</i>

(54) Title: HIGH SPEED CURTAIN COATING PROCESS AND APPARATUS



(57) Abstract

In a process of curtain coating, the use of very high coating speeds is facilitated by application to the surface of the object to be coated of a predetermined high level of electrostatic polar charge. The level of charge which is effective to promote the desired uniformity of coating with minimum formation of coating defects is directly related to the coating speed, so that increasingly higher levels of charge are needed as coating speed is increased. The process is particularly useful for coating photographic materials, such as multi-layer photographic films and papers.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT Austria	FR France	ML Mali
AU Australia	GA Gabon	MR Mauritania
BB Barbados	GB United Kingdom	MW Malawi
BE Belgium	HU Hungary	NL Netherlands
BG Bulgaria	IT Italy	NO Norway
BJ Benin	JP Japan	RO Romania
BR Brazil	KP Democratic People's Republic of Korea	SD Sudan
CF Central African Republic	KR Republic of Korea	SE Sweden
CG Congo	LI Liechtenstein	SN Senegal
CH Switzerland	LK Sri Lanka	SU Soviet Union
CM Cameroon	LU Luxembourg	TD Chad
DE Germany, Federal Republic of	MC Monaco	TC Togo
DK Denmark	MG Madagascar	US United States of America
FI Finland		

-1-

HIGH SPEED CURTAIN COATING PROCESS AND APPARATUS

Field of the Invention

This invention relates in general to the process of curtain coating and in particular to the use 5 of curtain coating in the manufacture of photographic materials such as photographic films and papers. More specifically, this invention relates to an improved curtain coating process which is especially adapted to high speed manufacturing operations that are capable of 10 achieving the high degree of precision that is essential in the photographic field, and to apparatus for use in such process.

Background of the Invention

Among the many known methods of coating 15 photographic materials there are two which meet the extreme requirements of the photographic industry for coating uniformity, extreme thinness of layers, wide range in coating speed and especially the ability of applying a plurality of layers simultaneously. The 20 first method known as bead coating is described in Beguin in United States Patent No. 2,681,294 issued June 15, 1954 and in Russell, United States Patent No. 2,761,791 issued September 4, 1956. The latter patent pertains specifically to multi-layer coating in which 25 two or more layers of coating composition are simultaneously applied to a moving support in the manufacture of photographic materials. The second method, known as curtain coating, is described in Greiller, United States Patent No. 3,632,374 issued 30 January 4, 1972 and Hughes, United States Patent No. 3,508,947 issued April 28, 1970. The latter patent specifically pertains to a method of multi-layer curtain coating in which two or more layers of coating composition are simultaneously applied to a moving 35 support by a free-falling curtain in the manufacture of photographic materials.

-2-

The curtain coating method in particular has many advantages in the manufacture of photographic materials that require the application of coated layers of a precise thickness, with regard to both widthwise and lengthwise uniformity, onto a continuously moving support material. It is recognized that many of the advantages achieved by the curtain coating method result from the fact that the free-falling curtain can be formed by a slide hopper which is not in close proximity to the application locus on the moving support. The bead coating process continues to be in general use because it had become so highly developed before the advent of curtain coating in the manufacture of photographic materials. Investigation of bead coating for coating photographic materials was particularly directed to the coating zone where it was found that in order to establish an extremely stable process it was necessary to control two stabilizing forces which effected bead formation. Control and stabilization of the bead formation permitted the use of a wide latitude of coating speeds, layer viscosities and layer thicknesses. The stabilizing forces are first, a pressure differential (suction) applied across the coating bead at the application locus as disclosed in Beguin U. S. 2,681,294 and, secondly, an electrostatic charge differential applied just prior to the application locus as described in Nadeau, United States Patent No. 2,952,559 issued September 13, 1960. Thus, both a pressure differential and an electrostatic charge serve to hold the bead within the coating zone. In a bead coating process, forces which act toward the web, such as those provided by a pressure differential or an electrostatic charge, aid in stabilizing the bead and maintain it in wetting contact with the moving web. In a curtain coating process, however, no bead is ever

-3-

formed and the mechanism of the coating action is distinctly different. Thus, for example, in a curtain coating process, the curtain is free-falling and impinges on the moving support with considerable
5 momentum to provide a sufficient force to stabilize the application locus and insure a uniform wetting line on the moving support. The required momentum is obtained by appropriate selection of the curtain flow rate and the height of free fall.

10 The preferred method for obtaining a uniform electrostatic force at the coating application point in bead coating is to form a bound polar charge on the support at a uniform level. With a bound charge there are equal and opposite electrostatic charges on the two
15 surfaces of the support. To retain the charge on the support until the coating application locus is reached requires that the support be a dielectric material having a very high resistivity. As the charged support passes over the grounded coating roll, the side of the
20 support adjacent to the coating roll mirrors a charge on the coating roll surface which effectively neutralizes the charge on the support in contact with the coating roll surface and creates the equivalent of a net charge on the surface of the support being coated. This
25 creates an electrostatic field at the coating application locus between the surface of the support and the grounded hopper lip. When a moving support with a net charge on the surface to be coated is passed over a grounded coating roller the electrostatic field of the
30 charge is effectively neutralized by the charge mirrored on the grounded coating roll surface.

It is extremely difficult, however, to obtain a uniform electrostatic field at the coating application locus and all subsequent patent disclosures since the
35 disclosure of U.S. 2,952,559 are concerned with the

-4-

effects of combining suction and electrostatic polar charge forces. Attention is directed, for example, to U. S. 3,206,323. Other patents mention use of polar charge assist in the bead coating of photographic materials at 5 significantly lower coating speeds. These include U. S. Patent 3,470,417, U. S. Patent 3,670,203, and U. S. Patent 3,671,806. In addition, other patents disclose methods of measuring and controlling the electrostatic field so that a uniform charge of the required magnitude is obtained.

10 These include U.S. Patent 3,531,314, U.S. Patent 3,730,753, U. S. Patent 3,702,258, U.S. Patent 3,757,163 and U.S. Patent 3,549,406.

As discussed briefly above, the coating mechanisms involved in bead and curtain coating are 15 completely different. Besides the difference in forces used to stabilize the coating at the application locus, the effects of such coating variables as viscosity of the coating composition, flow rate per unit width of coating, and support surface smoothness are usually completely 20 different in a bead coating versus a curtain coating process. With bead coating, to increase the coating speed without affecting coating uniformity, the viscosity of the bottom layer must be reduced (by dilution) thereby increasing the wet coverage as disclosed in U.S. Patent 25 4,001,024. Also, a rough support surface such as a textured or matte surface becomes much more difficult to coat at high speeds. In all of these cases, when the coating speed is increased, the coating bead has a greater tendency to either break or become unstable, resulting in 30 cross lines in the coating or extensive entrainment of air bubbles in the coating at the support-coating interface. With a curtain coating process, just the opposite relationships to the above noted bead coating relationships are observed. When curtain coating failures 35 occur at high coating speeds they can often be avoided by

-5-

increasing the viscosity of the coating composition, or lowering the wet coverage of the bottom layer or coating a rough support. On the other hand, when curtain coating at high speeds, a high flow rate per unit width can often 5 result in the problem of "puddling" of the coating on the support, which commonly occurs when the curtain velocity at the application locus on the support is greater than the velocity of the support being coated. However 10 puddling can also occur when the support velocity is greater than the curtain velocity. Thus coating failure at high coating speeds seems to occur because the momentum of the curtain at the coating application locus is too 15 high.

In view of these directly conflicting 20 requirements resulting from radically different coating mechanisms involved in bead coating and curtain coating processes, it is indeed surprising that establishing a high level of an electrostatic polar charge on the surface of a support could achieve unexpected advantages in 25 curtain coating. While the use of a low level electrostatic field was well known and developed for the bead coating process, there was no recognition in the prior art that it might be useful in solving the problems that arise in high speed curtain coating of photographic materials. On the contrary, it was believed that such a 30 force would be of no benefit whenever there was adequate curtain momentum. The observed failure of curtain coating at high speeds seemed to occur because there was too much curtain coating momentum so applying an electrostatic force at the coating application locus would if anything have been expected to make the situation worse. Such a 35 force might possibly have been considered useful at low coating speeds when there was insufficient curtain momentum, but not when the curtain momentum was more than adequate.

-6-

While the applicant does not wish to be bound by any theoretical explanation of the manner in which his invention functions, it is believed that the electrostatic polar charge provides an attraction between the falling curtain and the support which is sufficiently strong to provide a uniform and defect free coating.

It is postulated that the coating defects encountered in curtain coating as the web speed is increased to very high levels result in part from the mechanism referred to herein as "insufficient viscous friction" force. The effect of "insufficient viscous friction" force is characterized by a defect which results from a multitude of entrained air bubbles between the coating and the support and the presence of longitudinal bands which result when droplets of coating composition form upstream of the application locus and coat out to provide such bands. The "insufficient viscous friction" force hypothesis is suggested by the inability to coat uniformly, because the coating solution viscosity is too low, the flow rate is too high, or the support surface is too smooth. The problems resulting from "insufficient viscous friction" force manifest themselves in curtain coating only at very high coating speeds such as at web speeds of about 250 centimeters per second or higher. In accordance with this invention, a predetermined high level of electrostatic polar charge is utilized to solve these problems in high speed curtain coating, as contrasted with known use of electrostatic polar charge in bead coating, which involves a distinctly different purpose, namely the purpose of stabilizing a coating bead. A high level of electrostatic polar charge apparently contributes a substantial attractive force which acts, in the appropriate direction, in the region where the curtain impacts the web, and thereby substantially increases the speed at which coatings can be successfully applied by the

-7-

curtain coating mechanism. More specifically, with the use of the appropriate level of electrostatic polar charge, it is possible to operate at very high coating speeds, with a particular set of operating parameters such as web smoothness, flow rate, coating composition viscosity, and curtain height, while still successfully meeting the very high quality standards of the photographic coating art.

As previously indicated, the high speed curtain coating process of this invention is carried out at web speeds which typically begin at about 250 centimeters per second or higher. Speeds of as high as about 1,000 centimeters per second, or more, can be effectively utilized with the aid of the appropriate level of electrostatic polar charge.

Summary of the Invention

An object of the present invention is to provide a curtain coating process and apparatus for coating a moving object at very high coating speeds.

The above described object of the present invention can be attained by a process and apparatus for coating an object with liquid coating composition in which an object is advanced along a path through a coating zone, and a free-falling curtain which is comprised of one or more layers of liquid coating composition and extends transversely of said path is impinged within said coating zone on a surface of said moving object to form thereon a coating comprised of one or more layers. The invention is directed to establishing an electrostatic polar charge, on the surface of said object to which said coating is applied, of a magnitude sufficient to insure the uniformity of said coating.

The invention is further directed to a process and apparatus for coating an object with liquid coating composition in which said object is advanced along a path

-8-

- through a coating zone, and a free-falling curtain which is comprised of one or more layers of liquid coating composition and extends transversely of said path is impinged within said coating zone on a surface of said
- 5 moving object to form thereon a coating comprised of one or more layers; wherein said object is advanced at a speed of at least 400 centimeters per second and an electrostatic polar charge is established on the surface of said object to which said coating is applied, the
- 10 magnitude of said charge being selected in accordance with the speed of said object so that the ratio of said charge at any point on said surface, measured in volts, to said speed, measured in centimeters per second, is at least 1 to 1.
- 15 The present invention is particularly suitable for the manufacture of a photographic element wherein a single layer or a plurality of layers of liquid photographic coating composition are formed into a free-falling curtain which extends transversely of a web advanced along a path and said curtain impinges within a coating zone on said web, to form a single or multi-layer coating. The improvement comprises advancing said web at a speed of at least 400 centimeters per second and establishing an electrostatic polar charge on the surface
- 20 of said web to which said coating is applied, the
- 25 magnitude of said charge being selected in accordance with the speed of said web so that the ratio of said charge at any point on said surface, measured in colts, to said speed, measured in centimeters per second, is at least 1 to 1.
- The object of the invention is further attained by a curtain coating apparatus wherein the means for forming the free-falling curtain comprises a multiple slide hopper, wherein the electrostatic polar charge on
- 35 the support is a bound or polar charge and said means for

-9-

establishing an electrostatic charge is applied just prior to the coating zone and comprises a grounded backing roll and at least one grid-controlled ionizer.

Brief Description of the Drawings

5 FIG. 1 is a schematic illustration of the apparatus for applying a predetermined level of electrostatic polar charge to the surface of a web and thereafter curtain coating the web surface with a liquid coating composition.

10 FIG. 2 is a graph relating electrostatic polar charge level and coating speed in a typical curtain coating process for the manufacture of a photographic material.

15 FIG. 3 is a graph relating flow rate of coating composition and coating speed in a typical curtain coating process for the manufacture of a photographic material.

Description of the Preferred Embodiments

The invention is described herein with particular reference to the coating of photographic materials. This field of coating involves highly precise operations, so that the invention is especially beneficial in this field. However, the invention is in no way limited to use in the coating of photographic materials and can be advantageously employed in any curtain coating operation in which it is desired to achieve very uniform coating at very high rates of speed. Both single layer and multiple layer curtain coating processes benefit greatly from the electrostatic polar charge.

The curtain coating problems which this invention solves occurs only at very high coating speeds, such as at web speeds which are typically above 250 centimeters per second. In accordance with this invention, a predetermined high level of electrostatic polar charge is utilized to solve these problems in high speed curtain coating, as contrasted with the prior art use of

-10-

electrostatic charge in bead coating, which involves the use of electrostatic charge for a distinctly different purpose, namely the purpose of stabilizing a coating bead. In the preferred embodiments of this invention the 5 electrostatic polar charge at the application point is obtained by using a support with a high level of bound or polar charge and a grounded coating roll. Such use of a predetermined high level of electrostatic polar charge in curtain coating is frequently referred to herein, for 10 convenience, as the use of "polar charge assist," in the sense that it directly assists in achieving effective coating. A high level of electrostatic polar charge apparently contributes a substantial attractive force which acts, in the appropriate direction, in the region 15 where the curtain impacts the web, and thereby substantially increases the speed at which coatings can be successfully applied by the curtain coating mechanism. More specifically, with the use of the appropriate level 20 of electrostatic polar charge, it is possible to operate at substantially higher coating speeds, with a particular set of operating parameters such as web texture, flow rate, coating composition viscosity, and curtain height, while still successfully meeting the very high quality standards of the photographic coating art.

25 As previously indicated, the high speed curtain coating process of this invention is carried out at web speeds which are typically above 250 centimeters per second. Speeds of as high as about 1,000 centimeters per second, or more, can be effectively utilized with the aid 30 of the appropriate level of electrostatic polar charge.

Any type of curtain coating apparatus can be used in the present invention. Thus, for example, the coating apparatus can be a curtain coating hopper of the overflow weir type, the pressure extrusion type, the slide type, or 35 the slide-extrusion type. However, slide hoppers are

-11-

particularly preferred, especially for photographic coating operations. The coating apparatus can be adapted to carry out single-layer coating or it can be of the type with which a plurality of layers are simultaneously 5 coated. It can be adapted to carry out full width coating or to carry out coating of abutting or non-abutting stripes as described, for example, in Research Disclosure, Item 17553, Volume 175, November, 1978.

The process of this invention can be utilized to 10 coat any material or mixture of materials which can be put in liquid form, for example, in the form of a solution, a dispersion, or a suspension. In many instances where this method finds application, the coating composition is an aqueous composition but other liquid vehicles, of either 15 an organic or inorganic nature, can also be utilized and are fully within the contemplation of this invention. When multiple layers are coated, the respective layers can be formed of the same or different liquid coating compositions and these coating compositions can be either 20 miscible or immiscible with one another.

As indicated hereinbefore, the process of this invention is especially useful in the photographic art for manufacture of multi-layer photographic elements, i.e., elements comprised of a support coated with a plurality of 25 superimposed layers of photographic coating compositions. The number of individual layers may be as high as ten or more. In the photographic art, the liquid coating compositions utilized are usually aqueous compositions but organic compositions can also be employed. The individual 30 layers applied in the manufacture of photographic elements must be exceedingly thin, i.e., a wet thickness which is a maximum of about 0.015 centimeter and generally is far below this value and may be as low as about 0.0001 centimeter. In addition the layers must be of extremely 35 uniform thickness, with the maximum variation in thickness

-12-

uniformity typically being plus or minus two percent and in some instances as little as plus or minus one-half percent.

The process of this invention is suitable for use
5 with any liquid photographic coating composition and can be employed with any type of photographic support and it is, accordingly, intended to include all such coating compositions and supports as are utilized in the photographic art within the scope of these terms, as
10 employed herein and in the appended claims.

Useful photographic supports include film base, e.g., cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polycarbonate film, polystyrene film, polyethylene terephthalate film and other polyester
15 films; paper; glass; cloth; metal; and the like. Paper supports coated with alpha-olefin polymers, as exemplified by polyethylene and polypropylene, or with other polymers, such as cellulose organic acid esters and linear polyesters, may also be used if desired.

20 The term "photographic" normally refers to a radiation-sensitive material, but not all of the layers applied to a support in the manufacture of photographic elements are, in themselves, radiation-sensitive. For example, subbing layers, pelloid protective layers, filter
25 layers, antihalation layers, etc. are often applied separately and/or in combination and these particular layers are not radiation-sensitive. The present invention relates also to the application of such layers, and the term "photographic coating composition" as employed
30 herein, is intended to include the composition from which such layers are formed. Moreover, the invention includes within its scope all radiation-sensitive materials, including electrophotographic materials and materials sensitive to invisible radiation as well as those
35 sensitive to visible radiation.

-13-

More specifically, the photographic layers are coated according to the process of this invention can contain light-sensitive materials such as silver halides, zinc oxide, titanium dioxide, diazonium salts, 5 light-sensitive dyes, etc., as well as other ingredients known to the art for use in photographic layers.

Various types of surfactants can be used to modify the surface tension and coatability of photographic coating compositions in accordance with this invention. 10 Useful surfactants include saponin; non-ionic surfactants such as polyalkylene oxides, e.g., polyethylene oxides, and the water-soluble adducts of glycidol and alkyl phenol; anionic surfactants such as alkylaryl polyether sulfates and sulfonates; and amphoteric surfactants such 15 as arylalkyl taurines, N-alkyl and N-acyl beta-amino propionates; alkyl ammonium sulfonic acid betaines, etc.

Aqueous photographic coating compositions typically contain a hydrophilic colloid. Examples of useful hydrophilic colloids include proteins, e.g. 20 gelatin, protein derivatives; cellulose derivatives, polysaccharides such as starch; sugars, e.g., dextran; plant gums; etc.; synthetic polymers such as polyvinyl alcohol, polyacrylamide, and polyvinylpyrrolidone; and other suitable hydrophilic colloids such as are disclosed 25 in U.S. patent No. 3,297,446. Mixtures of the aforesaid colloids may be used if desired.

In a preferred embodiment of the present invention, the coating compositions are gelatin silver halide emulsions. Emulsions containing a wide variety of 30 silver salts can be used, such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide, silver bromoiodide or silver chloroiodide. Conventional addenda such as, for example, hardening agents, antifoggants, stabilizers, matting 35 agents, plasticizers, developing agents, and the like, can

-14-

be included in the emulsions. For use in color photography, the emulsions can contain color-forming couplers or can be emulsions adapted to be developed in solutions containing color-forming couplers or other
5 color-generating materials.

Apparatus which can be used, in accordance with this invention, to impact a predetermined high level of electrostatic polar charge to a web surface is described in United States patents 3,470,417 and 3,730,753 and in
10 Research Disclosure, Item 16974, May 1978 (published by Industrial Opportunities Ltd., Homewell, Havant Hampshire, P09 1EF, United Kingdom), the disclosures of which are incorporated herein by reference. Apparatus which can be used for the coating of single or multiple layers by the
15 curtain coating process is described in U. S. patent 3,508,947 to Hughes and U. S. patent 3,632,374 to Greiller, the disclosures of which are incorporated herein by reference.

Curtain coating hoppers employed in the practice
20 of this invention are typically equipped with edge guides to guide the free-falling curtain and define its width. Useful edge-guiding methods include the use of edge guides which ride on the web, as described in the aforesaid
25 patents to Greiller and Hughes, and the use of "liquid edge-guiding" techniques as described in Research Disclosure, Item 17553, Volume 175, November, 1978.

Under typical curtain coating conditions used in the manufacture of photographic materials, there is usually little to be gained from using polar charge assist
30 at coating speeds below about 250 cm/sec since the use of polar charge assist at such speeds will ordinarily have no substantial effect on coating uniformity or other means can be used to achieve satisfactory coating uniformity.

In addition to the level of electrostatic polar
35 charge, there are many other factors which influence the

-15-

curtain coating process, including the web speed, the curtain height, the viscosity of each layer, the flow rate of each layer, the surface tension, the application point on the coating roll, and the nature of the web material.

- 5 All of these factors interact in a highly complex manner and all can significantly influence high speed coating.

In referring herein to the application point, reference is made to the angle, either positive or negative, by which the plane defined by the free-falling 10 curtain deviates from the mid-point of the coating roll which supports the web. Too great a departure from the mid-point can result in undesirable disturbance of the curtain coating process, with resulting formation of the coating defects.

15 The process of this invention involves the application of an electrostatic polar charge at a predetermined high level sufficient to be effective in enhancing the uniformity of coating which results from the action of a free-falling curtain of liquid coating 20 composition impacting on the surface to be coated. It is thus clearly distinguishable from the curtain coating of a web or other object which may have acquired an irregular electrostatic charge pattern or a low level of electrostatic charge. Such accumulation of irregular 25 and/or low level electrostatic charge can result from various causes. For example, the conveyance of a web support over a series of rollers can result in the generation of an irregular electrostatic charge pattern on the web surface. Also, the corona-activation of the 30 surface of a web for the purpose of promoting coatability can result in the acquisition by the web surface of an irregular electrostatic charge pattern. However, such charge patterns are not effective in overcoming the curtain coating problems solved by this invention, since 35 the solution of these problems requires the presence of

-16-

electrostatic polar charge on the surface to be coated which is at a level equal to or greater than what was known to be an effective minimum level — typically a level of at least 400 volts — at substantially all points
5 on the surface of the support to be coated.

In a preferred embodiment of the present invention, the web, or other object to be coated, is advanced through the coating zone at a speed of 400 centimeters per second or higher and an electrostatic
10 polar charge is established on the surface to be coated at a level such that the ratio of the charge at any point on the surface, measured in volts, to the speed, measured in centimeters per second, is at least 1 to 1. Thus, for example, in coating at a speed of 400 centimeters per
15 second one would use a charge level that is at least 400 volts, but could be well above 400 if necessitated by other factors such as, for example, the use of a support which has a surface texture with which it is especially difficult to achieve coating uniformity. In a
20 particularly preferred embodiment of the invention, the level of electrostatic polar charge, in volts, is made equal to or greater than the web speed in centimeters per second plus 200 volts, e.g., for a 400 cm/sec web speed a polar charge level of 600 volts or more.

25 In the process of this invention, the upper limit to the level of polar charge that can be utilized is dictated by practical considerations involved in the design and construction of the charge generating apparatus and by the requirement that the level not be so great as
30 to have detrimental effects on the photographic emulsion or other coating composition.

In the preferred embodiments of the present invention, a level of polar charge is established which is substantially uniform over the entire web surface. In
35 other embodiments, it is advantageous for certain regions

-17-

of the web surface to be provided with a higher level of polar charge than other regions in order to promote the objective of coating uniformity. Thus, for example, in some curtain coating processes, the web is adapted to

5 extend beyond the edges of the coating roll, i.e., the web is wider than the width of the coating roll and therefore overhangs it. This may be done, for example, to reduce the tendency for the coating roll to become fouled with coating composition. In these processes, a problem can

10 arise in achieving uniform coating on the overhanging regions of the web. In particular, polar charge is less effective on the overhanging regions of the web than on the remainder of the web surface, apparently because, in the overhanging regions, there is no coating roll behind

15 the web to provide an electrical ground. For this reason, it is desirable to establish a higher level of polar charge over the regions of the web which overhang the coating roll than over the remainder of the web surface. This can be readily accomplished in the process of this

20 invention by providing supplementary charging means which apply supplementary polar charge to only the regions of the web which overhang the coating roll. Thus, for example, after the web is passed beneath a charging means which applies polar charge over the entire surface

25 thereof, and before it receive the coating composition, it is passed beneath a second charging means which applies polar charge only to the regions of the web which will overhang the coating roll. The charge applied in these regions must be of the same polarity as that applied over

30 the entire web surface and is preferably at a voltage level that is two to three times as great. By way of illustration, if a polar charge of 800 volts is applied over the entire web surface, then the supplementary polar charge applied to the overhanging regions is

35 advantageously about 1600 to about 2400 volts.

-18-

An alternative technique for use in processes in which the web overhangs the coating roll is to charge the entire web surface, including the overhanging regions, to a uniform polar charge level that is substantially higher
5 than that needed for the particular coating speed and coating condition employed, to thereby provide a level of polar charge which is adequate to ensure uniform coating on the overhanging web regions as well as over the remainder of the web surface. This means, of course, that
10 there will be a higher level of polar charge over the remainder of the web surface than the minimum level that is needed, but this is usually not objectionable.

The increase in coating speed that can be achieved by use of the process of this invention is
15 remarkable. Thus, for example, it is feasible to double the coating speed, as compared to the maximum speed that can be used without the use of significant levels of polar charge assist, while maintaining equal coating quality.

Referring now to the drawings, FIG. 1
20 schematically illustrates the coating process of this invention utilizing a multiple-slide hopper to simultaneously coat three layers of liquid coating composition on a web support. As shown in FIG. 1, web 10 is unwound from supply roll 12 and then passes around
25 tension roller 14 and over grounded metal roll 16 where it receives a uniform electrostatic polar charge of the appropriate level. The apparatus for generating the electrostatic polar charge is of the grid-controlled ionizer type. A first such ionizer comprises grid
30 elements 18 in association with a series of conductive elements 20, such as tungsten rods or wires. Grid 18 is connected to DC power supply 22 while conductive elements 20 are connected to DC power supply 24. A second ionizer comprises a grid 26 connected to DC variable power supply
35 28 and conductive elements 30 connected to DC variable

-19-

power supply 32. The function of the first ionizer is to eliminate any variations in polar charge on the surface of the incoming web. A high voltage direct current power supply provides a 15,000 volt potential to conductive
5 elements 20. This high voltage ionizes the atmosphere and the charged ions are accelerated toward web 10 through grid 18. Web 10 is charged to a uniform level determined by the power supply voltage to grid 18. Once the web reaches the grid potential, the ions are no longer
10 accelerated between the grid and the web surface and a uniform polar charge level is present on the web surface. The second ionizer serves to boost the uniform potential to a higher level and controls this level. This function is accomplished using variable output power supplies. The
15 output voltage is controlled electrically with a feedback loop comprising an electrostatic voltmeter 34 which measures the voltage on the web. By means of control circuits 36, this voltage is compared to a reference voltage and the power supply output voltage is either
20 raised or lowered automatically to keep a constant voltage level on web 10.

After web 10 has been brought to a desired uniform level of electrostatic polar charge, it passes around guide rolls 40, 42, 44, 46 and 48 and then over a
25 grounded coating roll 50 where it is coated with a three-layer coating of liquid coating composition, e.g., three different photographic emulsions, by means of multiple-slide curtain coating hopper 52 which receives the emulsions from a suitable supply source (not shown)
30 and generates free-falling curtain 54 that impinges on web 10. After passing over coating roll 50, web 10 is directed through drying chamber 56, where the emulsion layers are dried by contact with air or other gaseous medium maintained at an elevated temperature, and then
35 directed around guide roll 58 and wound onto take-up roll 60.

-20-

FIG. 2 relates the level of electrostatic polar charge required to give uniform coating with the coating speed for a typical curtain coating process in which a gelatin silver halide photographic emulsion is coated on 5 the surface of a web. The curve shown in FIG. 2 is representative for the coating conditions which follow, whereas a different set of coating conditions would result in a shift in the curve:

Curtain height - 12.5 centimeters
10 Curtain flow rate - 1.5 to 6 grams
per second per centimeter of curtain width
Viscosity of coating composition - 60
centipoise
Web surface - glossy polyethylene
15 Application point - minus 15 degrees.

Uniform coating is achieved in the region to the left of the curve, while a non-uniform coating that would not be useful in photographic manufacturing operations results in the region to the right of the curve. In other 20 words, the curve represents the transition between satisfactory coating and coating failure.

As indicated in FIG. 2, no polar charge assist is required to prevent coating failure at coating speeds up to about 250 cm/sec. In the region of coating speeds 25 between about 250 and about 400 cm/sec, the curve indicates a gradually increasing need for polar charge assist. Usually however, no polar charge assist is applied at speed levels between 250 and about 400 cm/sec because other means would be used to achieve satisfactory 30 coating uniformity. The slope of the curve decreased with further increase in coating speed. It should be noted that the ratio of the charge, measured in volts, to the speed, measured in centimeters per second, must be at least 1 to 1 to achieve uniform coating over a speed range

-21-

of 400 to 800 cm/sec with the particular coating conditions employed. The preferred embodiment of the invention may require additional electrostatic charge on the order of an additional 200 volts, e.g., for a 400
5 cm/sec web speed a polar charge level of 600 volts or more may be necessary.

FIG. 3 relates to the flow rate of coating composition per unit width of curtain with the coating speed. It describes a uniform coating region bounded by
10 identifiable regions in which poor quality coating occurs. The size and shape of the uniform coating region is dependent upon the curtain height, the coating composition viscosity, the application point, the nature of the web surface, and the level of electrostatic polar
15 charge assist. The unstable curtain region is the region where curtain flow rate per unit width is too low to produce a stable curtain. In this region, the curtain will split into a number of strands and thereby render the formation of a uniform coating impossible. The puddling
20 region represents conditions where the velocity of the curtain at the coating application point is greater than the web velocity. As a result, coating composition builds up behind the curtain and produces longitudinal streaks.

It is a particularly important feature of the
25 present invention that the uniform coating region can be substantially extended, for a given set of operating conditions, by the use of electrostatic polar charge assist, i.e., by the application of a sufficiently high level of electrostatic polar charge to the web surface.
30 Thus, by the use of electrostatic polar charge assist, the coating speed at which the onset of non uniform coating begins can be greatly extended. This enables a particular coating machine to be run at much higher speed, and thereby produce much more product, without any sacrifice
35 in the quality of the coating.

-22-

The following examples further illustrate the invention.

EXAMPLE I - By the bead coating method:

A multiple slide bead coating hopper similar to 5 that shown in U. S. 2,761,791 was used except that the hopper was set up to coat 7 layers simultaneously. The product coated was Ektacolor Paper which contains 7 separate layers. The wet thickness and viscosity of the 7 layers are tabulated in Table I.

10

Table I

<u>Layer</u>	<u>Wet Coverage Microns</u>	<u>Viscosity Centipoise</u>
Blue Sensitive (Bottom)	32 or 37	6.5 or 4.6
15 Interlayer	5	115
Green Sensitive	15	50
Ultraviolet Filter	7	63
20 Red Sensitive	14	32
Ultraviolet Filter	7	63
Overcoat	7	93

The viscosity of the bottom layer was adjusted 25 by dilution with water in order to obtain satisfactory coatability. Satisfactory coatability is defined as a stable coating system which is free of mottle, crosslines, micro bubbles and other coating defects. It was desired to attempt to coat this product at high 30 speed (400 cm/sec or higher) Table II shows the maximum coating speed achieved as a function of bottom layer viscosity and polar charge voltage. Both Matte (rough) surface and Glossy (smooth) surface supports were used as indicated in Table II.

35

-23-

Table II (Bead Coating Method)

Support Surface	(Maximum Coating Speed cm/sec)			
	No Polar Charge		350 Volts Polar Charge	
	Bottom Layer Viscosity	I (a) I (b)	Bottom Layer Viscosity	I (c) I (d)
5	6.5 cps	4.6 cps	6.5 cps	4.6 cps
Matte	300 cm/sec	350 cm/sec	350 cm/sec	400 cm/sec
Glossy	350 cm/sec	400 cm/sec	400 cm/sec	**

10 ** Polar charge not required to coat at 400 cm/sec.

For the matte surface support dilution of the bottom layer from 6.5 to 4.6 centipoise illustrated in Examples I(a) and I(b) resulted in an increase in maximum coating speed from 300 to 350 cm/sec while for a 15 glossy surface the increase was from 350 to 400 cm/sec.

When a polar charge of 350 volts was applied to the support prior to the coating zone as illustrated in Examples I(c) and I(d) the maximum coating speed for the matte surface support increased 50 centimeter/sec to a 20 maximum of 400 centimeters/sec for the very dilute bottom layer. This amounts to an improved maximum coating speed of approximately 14% to 17% depending upon the viscosity of the bottom layer when used with a matte surface. Application of a higher level of polar charge 25 above 350 volts was found not to appreciably improve bead coating speed.

For the glossy surface support a polar charge was not required to achieve satisfactory coatability at a speed greater than 400 cm/sec. Note that the glossy 30 surface support can generally be coated at approximately 50 cm/sec greater speed than the matte surface. Dilution of the bottom layer from 6.5 to 4.6 centipoise increased the maximum coating speed by 50 cm/sec for both types of supports.

-24-

It is well known that one of the advantages of using the curtain coating method for coating photographic materials over the known bead coating method is that the bottom layer does not have to be more dilute than the other layers. This is in contrast to the need in bead coating to use a very dilute bottom layer. In the above example 40% of the total water is in the bottom layer. This requirement tends to limit the speed at which a continuous coated web support can be dried. While the lowermost layer in a bead coating process is usually 10 centipoise or less and preferably 3 to 5 centipoise, the outer layers of a stable free falling curtain usually are 40 centipoise or higher. The advantages of coating with higher viscosity coating compositions are well known and discussed in Hughes U.S. Patent 3,508,947 one advantage being the significant decrease in the water load requirements on the drier which must continuously and uniformly dry the delicate photographic coating.

20 EXAMPLE II - Curtain Coating Method

A multiple slide curtain coating hopper similar to that shown in Figure 1 of U.S. Patent No. 3,508,947 was used except that the hopper was set up to coat 7 layers of coating compositions simultaneously. All 25 layer viscosities and wet coverages except for the bottom (blue sensitive) layer were identical to those shown in Table I. The bottom (blue sensitive) layer was replaced with a coating composition having a viscosity of 26 centipoise with a wet coverage of 20 microns. The 30 coating speed obtained using a matte and a glossy support surface are tabulated in Table III.

-25-

Table III (Curtain Coating Method)

Bottom Layer Viscosity 26 centipoise, wet coverage 20 microns

	Maximum Coating Speed cm/sec)	
	<u>No Polar Charge</u>	<u>700 Volts Polar Charge</u>

5

Support Surface

Matte	400 cm/sec	**
-------	------------	----

Glossy	300	At least 500 cm/sec
--------	-----	------------------------

10

** Polar charge not required to coat at 400 cm/sec.

The matte surface curtain coating data recorded in Table III should be compared with the matte surface bead coating data recorded in Table II. Whereas with bead coating it was necessary to use a polar charge of 350 volts to coat at a maximum speed of 400 cm/sec it was shown that such a speed could be achieved with the curtain coating method without the use of polar charge assist.

The coating requirements for a glossy surface support however were found to differ significantly and therefore could not be predicted based on prior knowledge of the bead coating method. For example, Table III shows that a maximum coating speed of only 300 cm/sec could be achieved for a glossy surface support using a 26 centipoise bottom layer when no polar charge assist was used. Table II relating to the bead coating method shows that for a glossy surface a maximum coating speed of 400 cm/sec could be achieved without use of a polar charge.

When a polar charge of 700 volts was applied to the coating surface prior to the application point the glossy surface support could be curtain coated at a speed of at least 500 cm/sec. This amounts to an

-26-

increase in the achievable curtain coating speed for the glossy support surface of at least 67% over that obtainable when no polar charge was used. Coating at higher speeds is possible when increasingly higher 5 levels of polar charge are used as shown in Figure 2.

Comparison of these examples shows that coating of photographic materials using the bead coating method which requires a very dilute (low viscosity) bottom layer has an upper limit for coating speed of about 400 10 cm/sec.

When coating a photographic material using the curtain coating process it was unexpectedly found that much higher coating speeds were possible. Although a very concentrated (higher viscosity) bottom layer is 15 applied when using the curtain coating it was unexpectedly found that application of a very high level of polar charge to coat a smooth web support such as a glossy support would result in coating speed well above 400 cm/sec.

20

25

30

35

-27-

What is claimed

1. In a process of coating an object with liquid coating composition in which said object is advanced along a path through a coating zone, and a free-falling curtain which is comprised of one or more layers of liquid coating composition and extends transversely of said path is impinged within said coating zone on a surface of said moving object to form thereon a coating comprised of one or more layers; the improvement which comprises establishing an electrostatic polar charge on the surface of said object to which said coating is applied, the magnitude of said charge being sufficient to insure the uniformity of said coating.
- 15 2. In a process of coating an object with liquid coating composition in which said object is advanced along a path through a coating zone, and a free-falling curtain which is comprised of one or more layers of liquid coating composition and extends transversely of said path is impinged within said coating zone on a surface of said moving object to form thereon a coating comprised of one or more layers; the improvement which comprises advancing said object at a speed of at least 250 centimeters per second and establishing an electrostatic polar charge on the surface of said object to which said coating is applied, the magnitude of said charge being selected in accordance with the speed of said object so that the ratio of said charge at any point on said surface, measured in volts, to said speed, measured in centimeters per second, is at least 1 to 1.
- 25 3. In a process for the manufacture of a photographic element in which a web is advanced along a path through a coating zone and a free-falling curtain which is comprised of a single layer of liquid

-28-

- photographic coating composition and extends transversely of said path is impinged within said coating zone on said web to form a coating thereon; the improvement which comprises establishing an
- 5 electrostatic polar charge, of a magnitude sufficient to enhance the uniformity of said coating, on the surface of said web to which said coating is applied.

4. In a process for the manufacture of a photographic element in which a web is advanced along a path through a coating zone and a free-falling curtain which is comprised of a single layer of liquid photographic coating composition and extends transversely of said path is impinged within said coating zone on said web to form a coating thereon, the improvement which comprises advancing said web at a speed of at least 400 centimeters per second and establishing an electrostatic polar charge on the surface of said web to which said coating is applied, the magnitude of said charge being selected in accordance with the speed of said web so that the ratio of said charge at any point on said surface, measured in volts, to said speed, measured in centimeters per second, is at least 1 to 1.

5. In a process for the manufacture of a photographic element in which a web is advanced along a path through a coating zone and a free-falling curtain which is comprised of a plurality of layers of liquid photographic coating composition and extends transversely of said path is impinged within said coating zone on said web to form a multi-layer coating thereon; the improvement which comprises establishing an electrostatic polar charge, of a magnitude sufficient to enhance the uniformity of said multi-layer coating, on the surface of said web to which said coating is applied.

-29-

6. The process as claimed in claim 5 in which said web is passed around a coating roll of lesser width than the width of said web so that said web overhangs said coating roll and the electrostatic polar charge 5 which is established on said web is of greater magnitude over the regions of said web surface which overhang said coating roll than over the remainder of said web surface.

7. In a process for the manufacture of a photographic element in which a web is advanced along a path through a coating zone and a free-falling curtain 10 which is comprised of a plurality of layers of liquid photographic coating composition and extends transversely of said path is impinged within said coating zone on said web to form a multi-layer coating 15 thereon, the improvement which comprises advancing said web at a speed of at least 400 centimeters per second and establishing an electrostatic polar charge on the surface of said web to which said multi-layer coating is applied, the magnitude of said charge being selected in 20 accordance with the speed of said web so that the ratio of said charge at any point on said surface, measured in volts, to said speed, measured in centimeters per second, is at least 1 to 1.

8. The process as claimed in claim 7 wherein 25 said web is composed of cellulose acetate film.

9. The process as claimed in claim 7 wherein said web is composed of polyethylene terephthalate film.

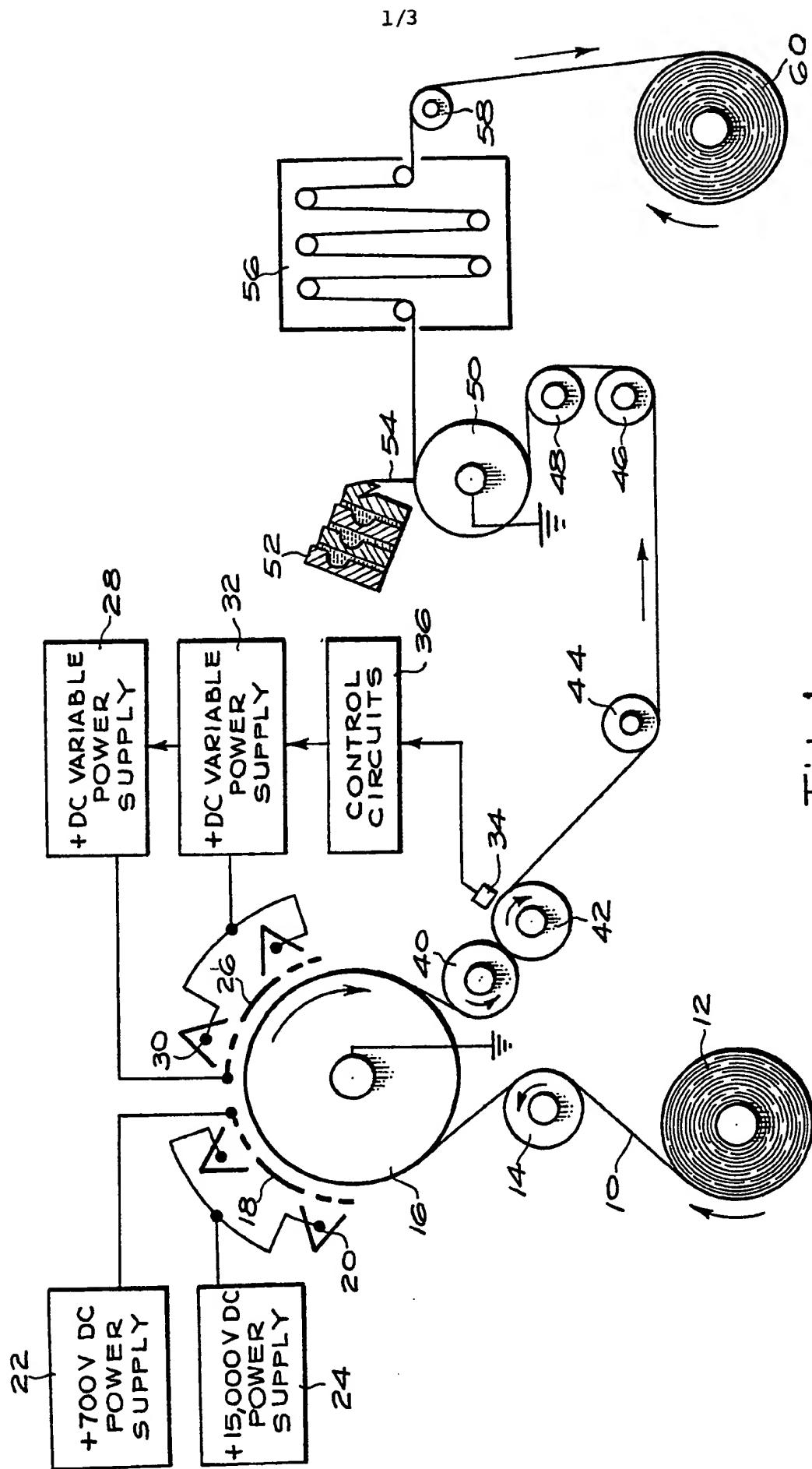
10. The process as claimed in claim 7 wherein said web is composed of polyethylene-coated paper.

30 11. The process as claimed in claim 7 wherein at least one of said layers is composed of a gelatin silver halide photographic emulsion.

12. The process as claimed in claim 7 wherein 35 the magnitude of said charge, measured in volts, is at least equal to the speed of said web, measured in centimeters per second, plus one hundred.

-30-

13. Curtain coating apparatus comprising:
means for advancing an object to be coated
along a path through a coating zone;
means for forming a free-falling curtain
5 comprised of one or more layers of liquid coating
composition which extends transversely of said path and
impinges within said coating zone on a surface of said
moving object to form thereon a coating comprised of one
or more layers; and
10 means for establishing an electrostatic
polar charge of a magnitude sufficient to enhance the
uniformity of said coating, on the surface of said
object to which said coating is applied.
14. Curtain coating apparatus as claimed in
15 claim 13 wherein said advancing means is capable of
advancing said object at a speed of at least 250
centimeters per second and said charge establishing
means is capable of establishing a electrostatic polar
charge of a magnitude such that the ratio of said
20 charge, measured in volts, to said speed, measured in
centimeters per second, is at least 1 to 1.
15. Curtain coating apparatus as claimed in
claim 14 wherein said object is a web and said means for
advancing said object is a web conveyance system capable
25 of operating at a controlled preselected speed.
16. Curtain coating apparatus as claimed in
claim 14 wherein the electrostatic charge is a bound or
polar charge said means for establishing an
electrostatic polar charge comprises a rounded backing
30 roll and at least one grid-controlled ionizer.
17. Curtain coating apparatus as claimed in
claim 14 wherein said means for forming a free-falling
curtain comprises a multiple-slide hopper.



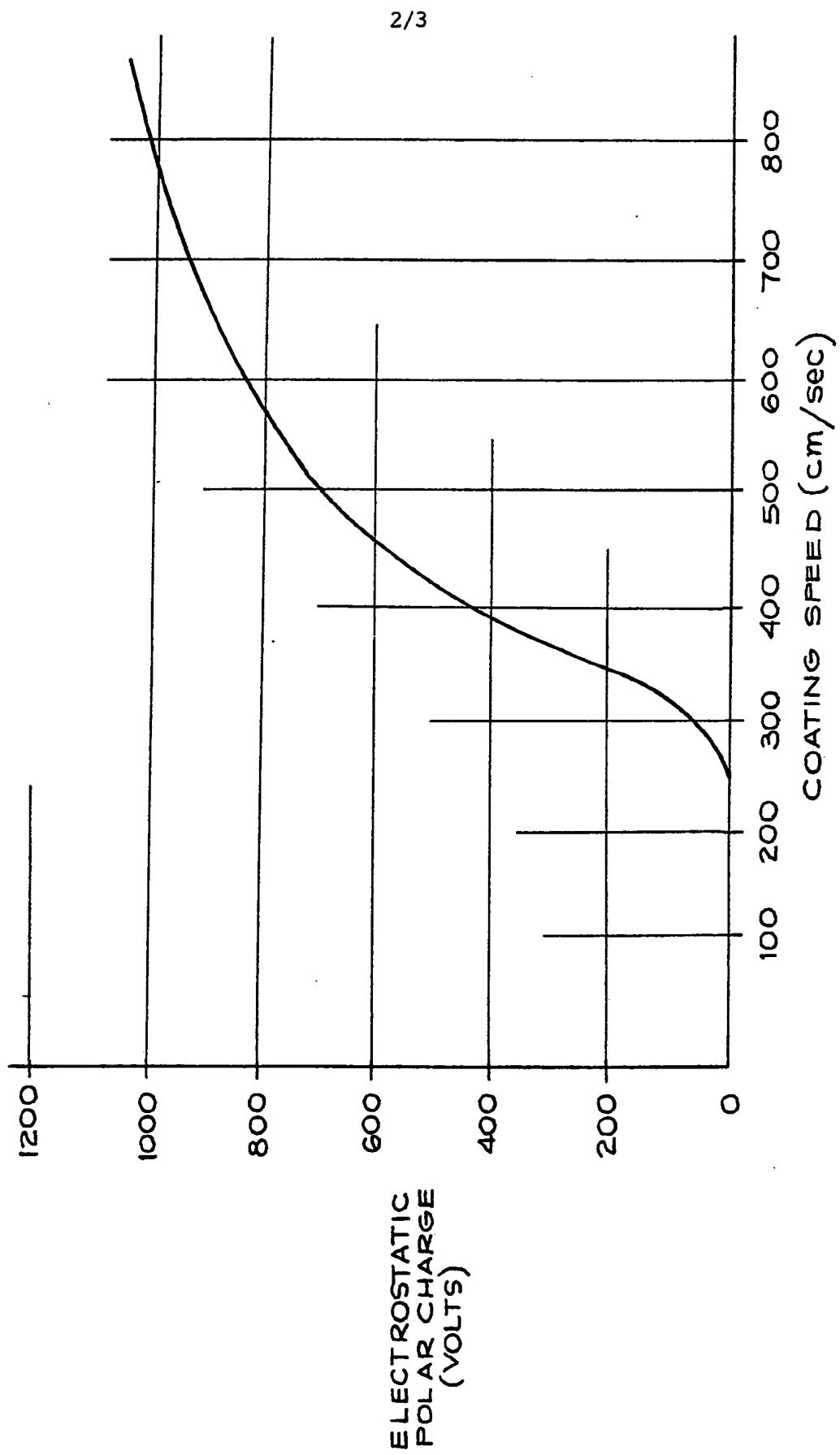


Fig. 2

3/3

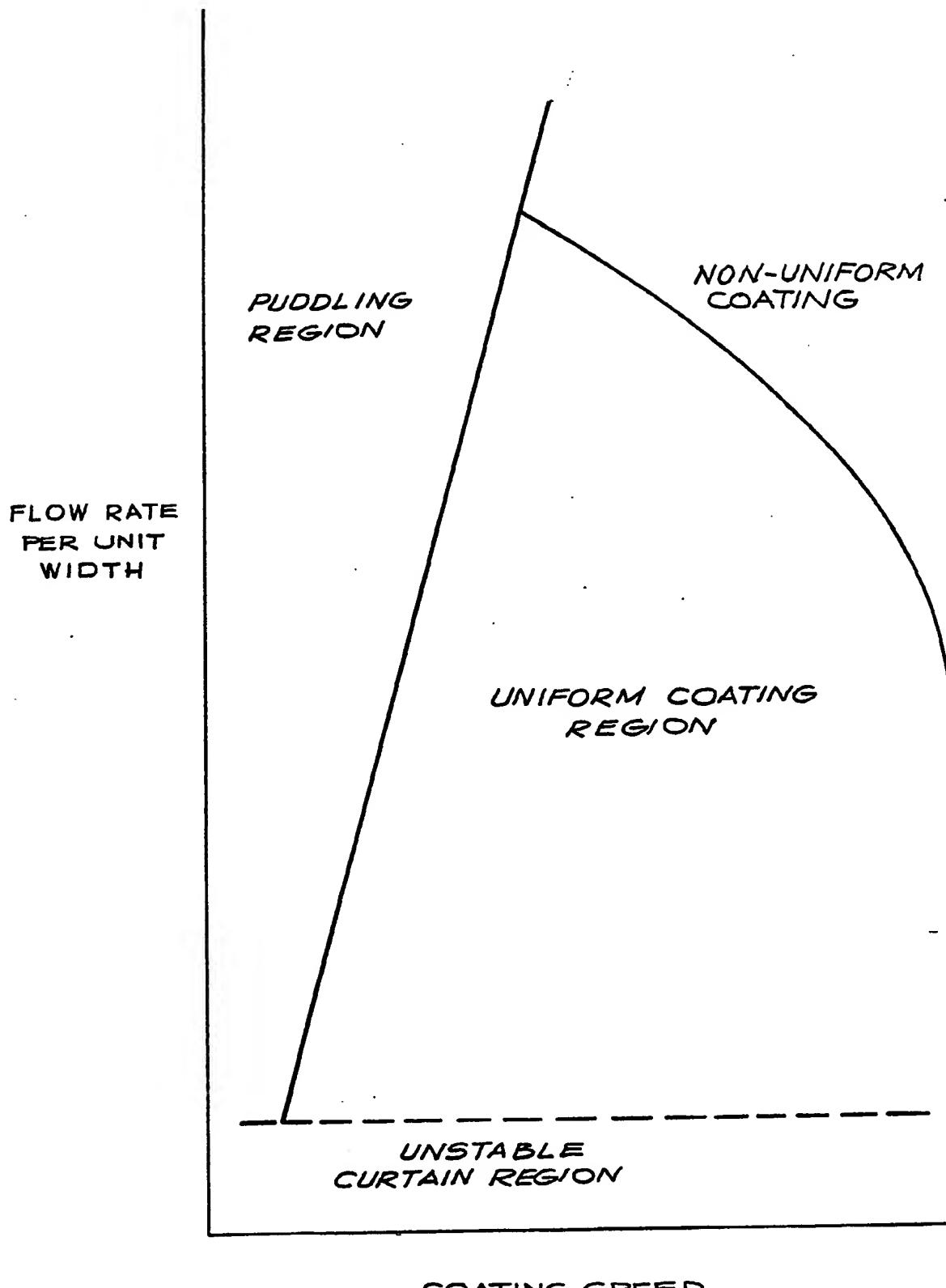


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/03190

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: G 03 C 1/74; B 05 D 3/14; H 05 F 3/04

II. FIELDS SEARCHED

Minimum Documentation Searched †

Classification System	Classification Symbols
IPC ⁴	G 03 C 1/74; B 05 D 3/14; H 05 F 3/00
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ‡	

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X, Y	EP, A, 0136606 (POLAROID) 10 April 1985, see the whole document	1-17
Y	US, A, 3757163 (C.B. GIBBONS et al.) 4 September 1973, see figures 1,2 cited in the application	1-17
Y	Patent Abstracts of Japan, vol. 10, no. 366 (C-390)(2423), 6 December 1986 & JP, A, 61161117 (FUJI PHOTO FILM CO LTD) 21 July 1986	1-17
Y	GB, A, 1166500 (FUJI PHOTO) 8 October 1969, see page 2, lines 38-48; claims	1-17
Y	US, A, 3462286 (W.F. DE GEEST et al.) 19 August 1969, see column 3, lines 55-63	1-17
A	EP, A, 0055983 (POLAROID) 14 July 1982, see abstract	1
A	FR, A, 1517840 (FUJI) 22 March 1968, see example 1	1-17

* Special categories of cited documents: ¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

28th July 1988

Date of Mailing of this International Search Report

26 AUG 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

D.F.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 8703190

SA 19929

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 18/08/88
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0136606	10-04-85	US-A-	4517143	14-05-85
		JP-A-	60095899	29-05-85
		CA-A-	1230372	15-12-87
US-A- 3757163	04-09-73	None		
GB-A- 1166500	08-10-69	DE-A,B	1577745	30-04-70
		FR-A-	1517840	
US-A- 3462286	19-08-69	None		
EP-A- 0055983	14-07-82	JP-A-	57167750	15-10-82
		US-A-	4457256	03-07-84
		CA-A-	1178134	20-11-84
FR-A- 1517840		GB-A-	1166500	08-10-69
		DE-A,B	1577745	30-04-70

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.